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14. ABSTRACT

In the past five years, we have proposed to use this grant to undertake research in the following areas:

- (1) Direct imaging of structural changes using ultrafast electron diffraction.
- (2) Neutral and ionic elementary reactions: high energy and solvation effects.

Our goal was to relate these dynamics to features of bonding and mechanisms and to explore the influence of high energy and solvation on reactivity. Theoretical studies in our group and in collaboration with colleagues elsewhere are an important part of this research.

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Final Performance Report

Air Force Office of Scientific Research

AFOSR Grant No. F49620-03-1-0070

**"Femtosecond Diffraction and Spectroscopy of Chemical
Reactions"**

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Contract/Grant Title: Femtosecond Diffraction and Spectroscopy of Chemical Reactions
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Objectives

Transient molecular structures are ephemeral, but fundamental to the understanding of mechanisms of reactions, energy storage and disposal, and properties in the different phases of matter, from gases to materials. The development of ultrafast electron and laser beam techniques to examine in real time the nature of the dynamics and structures on the femtosecond time scale has had major impacts in many fields. At Caltech, the laboratory for ultrafast diffraction and molecular imaging in the Center for Ultrafast Science and Technology is considered a national resource equipped with state of the art instrumentation. It is now possible to probe reactive structures with spatial resolution of picometer and temporal resolution of femtoseconds to picoseconds.

In the past five years, we have proposed to use this grant to undertake research in the following areas:

- (1) Direct imaging of structural changes using ultrafast electron diffraction.
- (2) Neutral and ionic elementary reactions: high energy and solvation effects.

Our goal was to relate these dynamics to features of bonding and mechanisms and to explore the influence of high energy and solvation on reactivity. Theoretical studies in our group and in collaboration with colleagues elsewhere are an important part of this research.

Accomplishments

In a series of papers published in *Science*, *JACS*, *JPC*, *ChemPhysChem*, and *PNAS*, we have developed ultrafast electron diffraction to a new level and for different applications. We are able to clock a change of chemical structure of *intermediates*. We believe this breakthrough is providing new opportunities in studies of energetic molecules and materials. For isolated systems we studied the structures involved in radiationless transitions, in proton transfer of organic reactions, and conformational changes of macromolecules.

Studies of novel ultrafast phenomenon in mesoscopic systems is another area of investigation. We reported previously on studies of oxygen anion clusters with first and second solvation shells and electrons in water clusters in a series of papers to *J. Chem. Phys.* The goal was to understand microscopic solvation under controlled conditions.

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We reported in *Science* (2005) on the mapping of dark structures in radiationless transitions. These processes are fundamental to all chemical and biological changes as through them systems transform radiative energy to heat. The following is a summary of our findings in the noted three areas taken from the abstracts of papers listed in the Publications section.

Ultrafast Electron Diffraction

Paper 5. The intermediate structures formed through radiationless transitions are termed "dark" because their existence is inferred indirectly from radiative transitions. We used ultrafast electron diffraction to directly determine these transient structures on both ground-state and excited-state potential energy surfaces of several aromatic molecules. The resolution in space and time (0.01 angstrom and 1 picosecond) enables differentiation between competing nonradiative pathways of bond breaking, vibronic coupling, and spin transition. For the systems reported here, the results reveal unexpected dynamical behavior. The observed ring opening of the structure depends on molecular substituents. This, together with the parallel bifurcation into physical and chemical channels, redefines structural dynamics of the energy landscape in radiationless processes.

Paper 6. In this contribution, we report studies in ultrafast electron diffraction (UED), with the aim of exploring new directions. The main focus is on the determination of complex structures and their dynamics with spatial and temporal resolutions sufficient to give an atomic-scale picture for the evolution in chemical or biological change. We also provide the theoretical framework for UED, and compare the experimental findings of UED to those predicted by density functional and charge density calculations. Selected applications are given in order to highlight phenomena related to concepts such as bifurcation of trajectories in dynamics, far-from-equilibrium coherent structures, and conformational robustness in biological structures. For the former two cases, we consider chemical systems, and, for the latter, we examine proteins of 200 atoms or more.

Paper 9. In this communication, we report on the use of ultrafast electron diffraction to determine structural dynamics of excited states and reaction products of isolated aromatic carbonyls, acetophenone and benzaldehyde. For a 266 nm excitation, a bifurcation of pathways is structurally resolved, one leading to the formation of the triplet state (quinoid structure) and another to chemical products: for benzaldehyde the products are benzene and carbon monoxide (hydrogen migration and bond rupture) while those for acetophenone are the benzoyl and methyl radicals (bond rupture). The refined structures are compared with those predicted by theory. These dark structures and their radiationless transitions define the reduced energy landscape for complex reactions.

Ultrafast Diffraction Techniques

Paper 17. Ultrafast electron microscopy and diffraction are powerful techniques for the study of the time-resolved structures of molecules, materials, and biological systems. Central to these approaches is the use of ultrafast coherent electron packets. The

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electron pulses typically have an energy of 30 keV for diffraction and 100-200 keV for microscopy, corresponding to speeds of 33-70% of the speed of light. Although the spatial resolution can reach the atomic scale, the temporal resolution is limited by the pulse width and by the difference in group velocities of electrons and the light used to initiate the dynamical change. In this contribution, we introduce the concept of tilted optical pulses into diffraction and imaging techniques and demonstrate the methodology experimentally. These advances allow us to reach limits of time resolution down to regimes of a few femtoseconds and, possibly, attoseconds. With tilted pulses, every part of the sample is excited at precisely the same time as when the electrons arrive at the specimen. Here, this approach is demonstrated for the most unfavorable case of ultrafast crystallography. We also present a method for measuring the duration of electron packets by autocorrelating electron pulses in free space and without streaking, and we discuss the potential of tilting the electron pulses themselves for applications in domains involving nuclear and electron motions.

Paper 19. In this contribution, we consider the advancement of ultrafast electron diffraction and microscopy to cover the attosecond time domain. The concept is centered on the compression of femtosecond electron packets to trains of 15-attosecond pulses by the use of the ponderomotive force in synthesized gratings of optical fields. Such attosecond electron pulses are significantly shorter than those achievable with extreme UV light sources near 25 nm (-50 eV) and have the potential for applications in the visualization of ultrafast electron dynamics, especially of atomic structures, clusters of atoms, and some materials.

Mesosopic Clusters

Paper 4. We directly observed the hydration dynamics of an excess electron in the finite-sized water clusters of water with $n=15, 20, 25, 30$, and 35 . We initiated the solvent motion by exciting the hydrated electron in the cluster. By resolving the binding energy of the excess electron in real time with femtosecond resolution, we captured the ultrafast dynamics of the electron in the presolvated ("wet") and hydrated states and obtained, as a function of cluster size, the subsequent relaxation times. The solvation time (300 femtoseconds) after the internal conversion [140 femtoseconds for $n=35$ was similar to that of bulk water, indicating the dominant role of the local water structure in the dynamics of hydration. In contrast, the relaxation in other nuclear coordinates was on a much longer time scale (2 to 10 pico-seconds) and depended critically on cluster size.

Paper 18. Two centuries ago solvated electrons were discovered in liquid ammonia and a century later the concept of the solvent cage was introduced. Here, we report a real time study of the dynamics of size-selected clusters, $n = 20$ to 60 , of electrons in ammonia, and, for comparison, that of electrons in water cages. Unlike the water case, the observed dynamics for ammonia indicates the formation, through a 100 fs temperature jump, of a solvent collective motion in a 500 fs relaxation process. The agreement of the experimental results-obtained for a well-defined n , gated electron kinetic energy, and time delay-with molecular dynamics theory suggests the critical and different role of the kinetic energy and the librational motions involved in solvation.

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Overviews

Paper 3. In this article we highlight recent developments of ultrafast electron diffraction and crystallography at Caltech. These developments have made it possible to resolve transient structures, both spatially (0.01 Angstrom) and temporally (picosecond and now femtosecond), in the gas phase and condensed media-surfaces, interfaces, and crystals-with wide-ranging applications. With the extension to ultrafast electron microscopy, discussed here and elsewhere, we present an overview of one major research area at our center.

Paper 8. In this review, we highlight the progress made in the development of 4D ultrafast electron diffraction (UED), crystallography (UEC), and microscopy (UEM) with a focus on concepts, methodologies, and prototypical applications. The joint atomic-scale resolutions in space and time, and sensitivity reached, make it possible to determine complex transient structures and assemblies in different phases. These applications include studies of isolated chemical reactions (molecular beams), interfaces, surfaces and nanocrystals, self-assembly, and 2D crystalline fatty-acid bilayers. In 4DUEM we are now able, using timed single-electron packets, to image nano-to-micro scale structures of materials and biological cells. Future applications of these methods are foreseen across areas of physics, chemistry, and biology.

Paper 20. In this perspective we highlight developments and concepts in the field of 4D electron imaging. With spatial and temporal resolutions reaching the picometer and femtosecond, respectively, the field is now embracing ultrafast electron diffraction, crystallography and microscopy. Here, we overview the principles involved in the direct visualization of structural dynamics with applications in chemistry, materials science and biology. The examples include the studies of complex isolated chemical reactions, phase transitions and cellular structures. We conclude with an outlook on the potential of the approach and with some questions that may define new frontiers of research.

The following publications detail the progress made on this grant and are available on line. Some of the findings have been communicated directly to our Program Officer, Dr. Michael Berman.

Archival publications (published) during reporting period:

- 1) R. Srinivasan, J. S. Feenstra, S. T. Park, S. Xu, and A. H. Zewail, "Direct Determination of Hydrogen-Bonded Structures in Resonant and Tautomeric Reactions Using Ultrafast Electron Diffraction," *J. Am. Chem. Soc.* **126**, 2266 (2004).
- 2) S. Xu, S. T. Park, J. S. Feenstra, R. Srinivasan, and A. H. Zewail, "Ultrafast Electron Diffraction: Structural Dynamics of the Elimination Reaction of Acetylacetone," *Journ. Phys. Chem. A* **108**, 6650 (2004).
- 3) A. H. Zewail, "Diffraction, Crystallography, and Microscopy Beyond 3D—Structural Dynamics in Space and Time," *Phil. Trans. R. Soc. A* **364**, 315 (2005).

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- 4) D. H. Paik, I-R. Lee, D.-S. Yang, J. S. Baskin, and A. H. Zewail, "Electrons in Finite-Sized Water Cavities: Hydration Dynamics Observed in Real Time," *Science* **306**, 672 (2004).
- 5) R. Srinivasan, J. S. Feensra, S. T. Park, S. Xu, and A. H. Zewail, "Dark Structures in Molecular Radiationless Transitions Determined by Ultrafast Diffraction," *Science* **307**, 558 (2005).
- 6) D. Shorokhov, S. T. Park, and A. H. Zewail, "Ultrafast Electron Diffraction: Dynamical Structures on Complex Energy Landscapes," *Chem. Phys. Chem* **6**, 2228 (2005).
- 7) J. S. Baskin and A. H. Zewail, "Ultrafast Electron Diffraction: Oriented Molecular Structures in Space and Time," *Chem. Phys. Chem* **6**, 2261 (2005).
- 8) A. H. Zewail, "4D Ultrafast Electron Diffraction, Crystallography, and Microscopy," *Annu. Rev. Phys. Chem* **57**, 65 (2006) - Review.
- 9) J. S. Feenstra, S. T. Park, and A. H. Zewail, "Excited State Molecular Structures and Reactions Directly Determined by Ultrafast Electron Diffraction," *J. Chem. Phys.* **123**, 221104 (2005).
- 10) P.-Y. Cheng, J. S. Baskin, and A. H. Zewail, "Dynamics of Clusters: From Elementary to Biological Structures," *Proc. Natl. Acad. Sci.* **103**, 10570 (2006).
- 11) S. Habershon and A. H. Zewail, "Determining Molecular Structures and Conformations Directly from Electron Diffraction Using a Genetic Algorithm," *Chem. Phys. Chem* **7**, 353 (2006).
- 12) I.-R. Lee, W. Lee, A. H. Zewail, "Primary Steps of the Photoactive Yellow Protein: Isolated Chromophore Dynamics and Protein Directed Function," *Proc. Natl. Acad. Sci.* **103**, 258 (2006).
- 13) S. T. Park, J. S. Feenstra, and A. H. Zewail, "Ultrafast Electron Diffraction: Excited State Structures and Chemistries of Aromatic Carbonyls," *J. Chem. Phys.* **124**, 174707 (2006).
- 14) D. H. Paik, J. S. Baskin, N. J. Kim, and A. H. Zewail, "Ultrafast Vectorial and Scalar Dynamics of Ionic Clusters: Azobenzene Solvated by Oxygen," *J. Chem. Phys.* **125**, 133408 (2006).
- 15) J. S. Baskin and A. H. Zewail, "Oriented Ensembles in Ultrafast Electron Diffraction," *Chem. Phys. Chem.* **7**, 1562 (2006).
- 16) Y. He, A. Gahlmann, J. S. Feenstra, S. T. Park, and A. H. Zewail, "Ultrafast Electron Diffraction: Structural Dynamics of Molecular Rearrangement in the NO Release from Nitrobenzene," *Chem. Asian Journ.* **1**, 56 (2006).
- 17) P. Baum, and A. H. Zewail, "Breaking Resolution Limits in Ultrafast Electron Diffraction and Microscopy," *Proc. Natl. Acad. Sci.* **103**, 16105 (2006).
- 18) I-R. Lee, W. Lee, and A. H. Zewail, "Dynamics of Electrons in Ammonia Cages, the Discovery System of Solvation," *Chem. Phys. Chem.* **9**, 83 (2008).
- 19) P. Baum and A. H. Zewail, "Attosecond Electron Pulses for 4D Diffraction and Microscopy," *Proc. Natl. Acad. Sci.* **104**, 18409 (2007).
- 20) D. Shorokhov and A. H. Zewail, "4D Electron Imaging: Principles and Perspectives," *Phys. Chem. Chem. Phys.*, Accepted for publication (2008).

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